In-Situ Polymerization of Maleic Acid in Presence of *Aloe vera* Gel for Development of Eco-Friendly Eri Silk based Handlooms

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Abstract

Polycarboxylic acid compounds such as butane-tetra-carboxylic acid, cyclopentane-tetra-carboxylic acid, and citric acid offer an environmentally friendly, non-toxic, and safe alternative to toxic formaldehyde condensate resin as a silk cross-linking agent. However, the sodium salts of phosphorus-containing mineral acids used as esterification catalysts with such polycarboxylic acids are not environmentally friendly because of their reported adverse effects on the aquatic environment and soil. Also, finishes based on such non-polymeric polycarboxylic acids cannot retain or improve the strength and moisture-regain characteristics of silk. Moreover, most polycarboxylic acids are too expensive for practical exploitation. In view of the above, the present work was aimed at establishing the optimum condition for the application of vinyl monomer containing carboxylic acid like maleic acid in presence of initiator and catalysts on silk fabric in the presence of ammonium persulphate as the free radical polymerization catalyst and trisodium citrate as the esterification catalyst. In this study, eri silk-based handloom fabrics were finished with *Aloe vera* gel and maleic acid as a cross-linking agent using the pad-dry-cure method. Water-soluble *Aloe vera* gel with varying concentrations of 5 to 15% (w/v) was also added in the finishing bath to add antibacterial activity to the fabric along with the anti-crease properties. Evaluation of attainable changes or improvements in the eri silk based handloom fabric properties in respect of tensile strength, wrinkle recovery, flexibility, antimicrobial, porosity and moisture regain on such treatments have been done. Besides this, changes in the chemical nature of silk fabric on such modifications have been studied by infrared (IR) spectroscopy and reported in this research article. The study proposes thermal curing system is conducive for in-situ polymerization of maleic acid in presence of *Aloe vera* for the development of eco-friendly eri silk based handlooms with antibacterial and anti-crease properties, without a significant loss in strength properties. The effects of the antimicrobial agent were assessed even after the 10 wash cycle.

Introduction

Silk is an important environment-friendly biodegradable protein fibre considered and identified to be the textile fibre of the future that supports most among the natural fibres the growing concept of sustainably in respect of its production from the silkworm. Silk fibre also has some other advantages viz. Its high strength, appreciable moisture regain low specific gravity, appreciable elastic recovery, and good thermal stability. Silk is primarily appreciated for its lustre, elegant appearances and soft feel particularly when the soluble globular protein or gum as it is called is removed from linear protein macromolecules of silk fibre. The draw black of silk fibre lies in its poor crease resistance (Yang and Li, 1992) and also susceptibility to attack by the microbial organism.

Silk is a structure less secretion in the form of a cocoon consisting of continuous filament and classified under two varieties namely domesticated and wild silk. The filament is smooth, lustrous, elastic and the length varies from cocoon to cocoon and from species to species. Silk principally consists of two portions as fibroin and sericin. Fibroin is the silk fibre usually coated with sericin the silk cover, in other words, sericin encloses fibroin in a continuous sheet. The composition of different silk type is shown in Table 1.Out of the silk varieties, eri is known as peaceful silk or ‘the poor man's silk’. Eri silk is highly valued not only for the environmental-friendly approach that is taken during its farming and production but also for its qualities. In the summer, it provides a cooling effect, whereas on colder days it provides warmth and a feeling of coziness. There is an old proverb in Assam ‘dair pani, erir kani’ which says that while yoghurt cools, eri cloth provides warmth. The slight imperfections of handspun yarn used to make eri textiles give them distinctive character silk (Chattopadhyay et al. 2018). Touching the smooth texture of these hand-woven textiles allows us to imagine the journey of its creation, a sensation we would like more people to discover and enjoy.

Eri silk is from 'attacus ricini' genus of silkworm. Major sources of eri silk are Assam, Meghalaya, Manipur and Mizoram. It is also available in Bengal, Orissa and Bihar. Eri-culture is a household activity practised mainly for protein-rich pupae, a delicacy for the tribal. The silk is used indigenously for the preparation of chaddars (wraps) for use by tribals. Eri silk fabric is a boon for those who practice absolute non-violence, not using any product obtained by killing any animal. That is why it is known as ‘ahimsa silk’. It has a textured surface with a delicate yet long-lasting feel. Eri silk also has very beautiful shades, cream or slightly reddish, which are determined by the food the worms eat. Apart from apparel usage, eri silk too could be used for functional textiles like anti-crease, anti-microbial and other properties for the home textiles and meditech segment of technical textiles. Especially, value addition of eri silk based handloom products is need of the hour. Nevertheless, this eri silk has excellent qualities: it is very strong, combining the elegance of silk with the comfort of cotton and the warmth of wool (Das et al. 2017). Eri silk is the most textured silk that needs a huge amount of preservation and care strategy. It has shorter fibres than the usually cultured silks. The shorter fibres of eri silk make it less durable. It is indeed one of the softest and purest forms of silk which is fancied by almost all the silk lovers' wardrobe. The silkworms give the eri silk a dull yellow, gold like sheen. However, apart from apparel usage, eri silk has also used for functional textiles.

The objectives of this study are to improve the anti-crease properties of silk using vinyl monomer containing carboxylic acid in presence of initiator and catalysts. Eri silk was treated with an aqueous liquor containing a polymer of a vinyl monomer containing acids has improved the anti-crease properties. Functional finishing is used to enhance the performance of the textiles products for their specific end uses. These finishes are usually based on surface-oriented applications to meet out the exact need of the customer. In addition to the anti-crease property, this study was carried out to extract the antimicrobial agent from *Aloe vera* gel with methanol and to explore the antimicrobial activity of *Aloe vera* gel extract on degummed silk fabric by way of incorporating water-soluble *Aloe vera* with varied concentrations of 5, 10% (w/v) and above in the finishing bath to impart antibacterial activity to the fabric along with the anti-crease characteristics. It is also aimed to produce eco-friendly anti-crease and antimicrobial eri fabric from *Aloe vera* gel extract and to safeguard the end-user from microorganisms contamination. Quantitative analysis is carried out to measure the antimicrobial activity against gram-positive Staphylococcus aureus (S. aureus) and gram-negative Escherichia coli (E. coli) bacteria. And then, the physical textile properties of treated and untreated eri fabrics such as crease recovery, fabric stiffness and strength were analyzed. The results demonstrate that the antimicrobial activity of *Aloe vera* gel treated fabric is excellent for both the gram-positive (S. aureus) and gram-negative (E. coli) bacteria. The results also reveal that the antimicrobial *Aloe vera* gel treatment does not affect the properties of degummed eri silk fabric.

Crease resistance finishing of cotton and silk textile using resins from amine formaldehyde condensates such as dimethylol dihydroxy ethylene urea (DMDHEU), dimethylol propylene urea (DMPU), resins result in some odd disadvantages in respect of relatively poor tensile strength retention despite significant improvement in wrinkle recovery. Such amine formaldehyde condensate resin finishes are also associated with the disadvantage of formaldehyde splitting during processing and use, endangering the health of processors and species and also as a probable carcinogen (Brodmann et al. 1990; Cao et al. 2000). Finishing of cotton and silk with polycarboxylic acids as formaldehyde-free finishing agent such as butane-tetra-carboxylic acid, cyclopentane-tetra-carboxylic acid appear to be much more prospective in this respect. Such compounds have evoked immense interest in the recent past because of their environment-friendly and non-toxic characters. However, such compounds are too expensive to be practically exploited and not widely available. Silk fabrics are often subjected to chemical finishing using cross-linking agents to convey easy-care properties. Amine formaldehyde condensate resin finishes are also associated with the disadvantages of formaldehyde splitting during processing and use, endangering the health of processors and users (Munshi et al. 2014). Though the cross-links contributed towards fabric's wrinkle resistance, also resulted in discolouration and impairment of fabric strength and other mechanical properties (Kang et al. 1998) cross-linking between phenolic -OH and primary hydroxyl groups, respectively of tyrosine and serine amino acids of silk macromolecular network causes fibre embrittlement that reduces the treated fabric's mechanical strength (Das and Munshi, 2006).

The sodium salts of phosphorous-containing mineral acid used as esterification catalyst with such polycarboxylic acid compounds are not environment friendly. Such catalysts containing phosphorous influence the reproduction of fish and favours a kind of seaweed growth that consumes a large amount of oxygen from water giving rise to eutrophication. Also, finishes based on such non-polymeric polycarboxylic acid cannot retain and/or improve the strength and moisture-regain characters of cotton and silk (Das et al. 2011; Das et al. 2015). However, report of the effect of polymerizable vinyl monomer for improvement in wrinkle recovery of cotton and silk fabrics are scanty. Carboxyl containing vinyl monomer like maleic acid under the influence of appropriate catalytic system shall produce anti-crease finishing on silk substrate (Das et al. 2014).

From the ancient periods, clothing ranks second topmost priority next to food. The use of textile for clothing is familiar to mankind from primitive age was gradually extended to household and domestic applications with progressive civilizations. Clothing that served mere protection has changed to ‘health-based clothing’. Now, there is a good deal of demand for the fabrics having functional/speciality finishing which is having resistance against microbes is the need of the hour. The application of antimicrobial textile finish included a wide range of textile products for the medical, technical, industrial, home furnishing and apparel sectors. At present, there is a lot of potential in antimicrobial finish application on textiles (Arai et al. 2001; Lim et al. 2004). This paper summarizes a comprehensive view of antimicrobial finishing and the required standard assessment.

Since the ancient period, man has always concern about his protection against which then leads to several developments in every field with regards to textile. The protective textile is assigned to cover the aspect of safety and security of human being in all respect. Increased global competition in developing advanced textile-based medical products has created many challenges for textile researchers and industrialists. The rapid growth in medical and wellness textiles has evolved many opportunities for the application of innovative functional finishes. Antimicrobial finished textiles with improved functionality find a variety of applications such as infection control, other health and hygiene applications. In the last few decades, research has been carried out in developing novel technologies to produce enhanced antimicrobial activity on textiles by using different synthetic antimicrobial agents such as triclosan, metal and their salts, organometallics, phenols and quaternary ammonium compounds. Although synthetic antimicrobial agents are very effective against a range of microbes and provide a durable effect on textiles, they are the cause of concern due to the associated side effects and ecological problems like water pollution. Hence, there is a need and demand for antimicrobial textiles based on eco-friendly agents which not only help to reduce the ill effects associated due to microbial growth on textile materials but also comply with the statutory requirements imposed by the regulating agencies. There is a vast resource of natural products with active antimicrobial ingredients amongst which the plant-based products cover a major range (Joshi et al. 2009). The healing power of some of the plant materials has been well-known and used since ancient times.

The major challenges in the application of natural products for textile application are most of these plant materials are complex mixtures of several compounds and also the composition varies in different species of the same plant. The durability, shelf life and antimicrobial efficiency of natural products are other issues of concern. To address these issues further research should be carried out in the area of bioactive textiles made from natural products, to make them a viable alternative to synthetic product based antimicrobial textiles. *Aloe vera* has been used as a skincare product for more than 2000 years. There are more than 350 *Aloe vera* species of the genus *Aloe* family which are available in various parts of the globe. Some of the important *Aloe vera* species are *Aloe arborescens, Aloe aristata, Aloe dichotoma, Aloe ngobitensis, Aloe variegate, Aloe wildii, Aloe barbadensis miller*, etc. Among all these varieties *Aloe barbadensis miller* is mostly used because of its excellent medicinal properties (El-tahlawy et al. 2005). In a study, it was found that the *Aloe* leaf contains over 75 nutrients and 200 active compounds, including 20 minerals, 18 amino acids and 64 vitamins (Ali et al. 2014). The main components of these constituents are glycoprotein, barbaloin, aloe-emodin, emodin, mannose-6-phosphate, polysaccharides, acemanan, aloesin, etc. The active ingredients of *Aloe vera* gel have a wide range of activities such as moisturizing, anti-inflammatory, antibacterial, antifungal, antiviral agent, anti-odour, etc. They also possess UV protective, antiprotozoal and wound healing properties (Alonso. 2016). The wound healing property of *Aloe vera* has been extensively studied (El-shafei et al. 2008). Glycoprotein and mannose-6-phosphate present in *Aloe vera* have good wound healing property (Choi and Chung 2003). Polysaccharides and barbaloin in *Aloe* gel are mainly responsible for their antimicrobial activity (Bang et al. 2007). The antifungal and antibacterial properties of *Aloe vera* can be exploited for medical textile applications, such as wound dressing, suture and other bioactive textiles.

In this context, it would be useful if we consider the mechanism of intended modification of eri silk with maleic acid following pad-dry-cure technique under the influence of ammonium persulphate used as the free radical polymerization catalyst and trisodium citrate used as esterification catalyst (Das et al. 2014). Hydroxyl groups of amino acid of silk are expected to bring about intended modifications under the sequence of reactions shown in Fig. 1. Such intended modification of silk fibre ultimately would lead to a notable gain in weight, and changes in the chemical nature and physical properties of silk during the overall process.

Reaction 1 producing maleic acid esters of silk would be the direct consequences of the action of trisodium citrate used as an esterification catalyst. The said esterification reaction would also expectedly lead to cross-linking of silk as mentioned in the reaction scheme 1. However maleic esters of silk as shown by the structures (i) and (ii) may then react further with hydroxyl groups of silk respectively leading subsequently to linking of silk via an ester bridge formed by the maleic acid moiety as shown by reaction 1 during the drying and curing step.

Influence of free radical catalyst $[(NH_4)_2S_2O_8]$ on the other hand in pad-dry-cure technique would cause graft copolymerization of maleic acid under the treatment condition ultimately leading to the grafting of poly (maleic acid) chain on the chain molecule of silk under the treatment condition with ultimate cross-linking of silk in addition to peroxodisulfate induced free radical homopolymerization of maleic acid; not shown in the scheme) is another distinct possibility. Such peroxodisulfate induced graft copolymerization and cross-linking would cause enhancement of carboxylic group content of the maleic acid-modified silk via maleic acid and improvement in wrinkle recovery of silk inconsequent to expected cross-linking of polymeric chains of silk. Under the influence of two catalysts taken together for the maleic acid curing of silk, all the reactions shown and discussed above are likely to take place simultaneously or successively leading to weight gain for the fabric system. Moreover, additional reactions leading to further graft copolymerization and esterification with consequent eventual complex network formation involving further unreacted hydroxyl groups of silk and also carboxyl groups and unsaturation of poly (maleic acid) moieties duly grafted to silk may also take place under the treatment condition leading to improved wrinkle recovery of maleic acid finished silk.

The microorganism which is unicellular in structure used to grow at a rapid pace under warmth and moisture. It grows rapidly in presence of humidity, heat and food sources whether it is gram-positive (S. aureus) and gram-negative (E. coli). The skin of human being is very much conducive to bacterial growth due to the acidic or basic nature of perspiration. After antimicrobial finishing, Silk fibres inhibit the supportive environment for microbial growth (Munshi and Majumdar, 2018; Ali et al. 2014).

In the present work, an attempt has been made to finish the eri silk with *Aloe vera* gel along with vinyl monomer containing carboxylic acid-containing vinyl comonomer cross-linking agent. The present work was undertaken to thermal curing of eri silk fabrics treated with maleic acid as a formaldehyde-free finishing agent along with *Aloe vera* gel to impart easy care and antimicrobial properties. Finishing agents comprised trisodium citrate and ammonium persulphate as a catalyst. The finished fabric was characterized by Fourier Transform Infrared Spectroscopy (FTIR) to understand the mechanism of attachment of *Aloe vera* gel with eri silk substrate in presence of maleic acid. The antibacterial property of *Aloe vera* gel finished fabric was evaluated against both gram-positive and gram-negative bacteria. The mechanism of destruction of both gram-positive and gram-negative bacteria by *Aloe vera* gel has also been established. This research article is mainly focused on the contemporary research on the usage of *Aloe vera* gel on silk towards their applications in numerous biomedical fields namely surgical gowns, drapes, wound-healing, burn treatment and some other useful purposes in the present scenario of Covid-19 pandemic outbreak in all over the world.

Experimental

Materials

Eri silk based handloom fabric with warp count 32 Ne (18 tex) and well count 30 Ne (20 tex) having an average area density of 92 gm^2 was used for the present study. In this experiment generally, we use silk, degummed eri silk fabric. Commercial grade maleic acid obtained from m/s micromoles India was used without any treatment. All other chemicals used like trisodium citrate, ammonium persulphate were of laboratory grade. *Aloe vera* gel was extracted from the *Aloe vera* trees locally available.

Methods

Degumming of silk

To remove silk gum from the raw eri silk fabric, later on, the fabric was degummed at 90^0C for 1 hour in an aqueous solution containing 20% soap and 2 grams per litre sodium carbonate at fabric to liquor ratio 1:20. Degummed fabric was washed using hot water and then cold washed and finally dried in air.

Application of maleic acid on silk

Pre-soaking of degummed silk fabric with ammonium persulphate solution of concentration 1% following an application of maleic acid monomers formulation on the pre-soaked silk fabric were performed separately by padding technique in a laboratory two bowl padding mangle. After two successive fabrics dipping in the maleic acid formulation, the pressure between the squeezing rollers was adjusted to enable an overall pick up of 100%.

The pH of the monomer solution was adjusted at different specified levels with the use of the required dose of soda ash and caustic soda. The aqueous monomers formulation usually contained a known dose of sodium tricitrate and *Aloe vera* gel with varied concentration of 5% to 15% (w/v), respectively. Finishing of silk with maleic acid with *Aloe vera* gel also rendered the silk fabric to impart antimicrobial property into silk. The padded squeezed fabrics were subjected to drying in an oven at 95^0C for (10-15) minutes. The dried fabrics were then cured at 140^0C for 5 minutes. Untreated and maleic acid-treated silk fabrics were assessed for change of the properties as listed below following standard procedures.

Determinations of moisture regain and weight gain after treatment

Moisture regain of the initial and treated silk fabrics was determined following a standard procedure mentioned in ASTM Standards, 1974. For the determination of weight gain upon finishing treatments using maleic acid, the finished fabric samples were first soap washed and then extracted under reflux in a water bath for 8-10 hours successively using water to ensure removal of traces of unreacted maleic acid monomer along with polymeric maleic acid that remains unbound to the chain molecules of silk fabric samples. The extracted fabric samples were then oven-dried to a constant weight (W_1) at 100^0C. The weight gain (%) was calculated based on the initial dry weight of degummed silk (W_2), using the following relationship: Weight gain= $(W_1-W_2) / W_2 \times 100$.

Tensile properties

Breaking strength of some selected fabric samples was measured in a Zwick 1445 CRT Universal Tensile Testing Machine, following the method prescribed by IS: 1969-1968 and described in Handbook of Tensile Testing, 1981. The results obtained were based on an average of 10 tests in the warp direction of each sample. The test strip specimens were ravelled to a size of 50mm x 20mm between the jaw of the machine, and the test was performed with a traverse speed of 100 mm min^{-1} at a pretension of 0.5N.

Determination of wrinkle recovery angle

The dry wrinkle recovery angle (warp+weft) of selected fabric specimen having size 25mm x 200mm was determined by a SASMIRA Wrinkle Recovery Tester following the method prescribed in ASTM-D-1295-67.

Porosity analysis

The porosity of untreated fabrics and treated fabrics are measured by a Capillary Flow Porometer (CFP-1100-AEHXL, PMI Inc.). All measurements are done by dry up/wet up test mode using distilled water to saturate the samples after the dry test. Minimum, maximum, average pore diameters and pore size distribution of all samples are measured following the Annual Book of Pore Size and Air Permeability of ASTM Standards, (1995).

Evaluation of antibacterial property of the textile fabric

Antibacterial susceptibility testing was done using the well diffusion assay, as prescribed by the National Committee for Clinical Laboratory Standards. The antibacterial activity was quantitatively assessed against gram-negative bacteria E. coli (Strain No.-ATCC 9637) and gram-positive bacteria S. aureus (Strain No.-ATCC 6538) according to the AATCC 100-2004 test method. The fabric samples with 2.5 ± 0.1 cm in diameter were placed in a 250 ml glass jar with a screw cap and absorbed with 1.0 ± 0.1 ml of bacterial inoculums. Then 100 ml of sterilized saline water (prepared by dissolving 0.85g of NaCl in 100 ml of distilled water) was added into the jar which was then shaken for 24 hours in a shaker at 100 rpm. After incubation over contact periods of 24 hours the solution was then serially diluted. The diluted solution was placed on nutrient agar and incubated for 24 hours at 37°C±2°C. Colonies of bacteria recovered on the agar plate were counted, and the per cent reduction of bacteria (R) was calculated by the following equation: $R\% = [(B - A)/B] \times 100$. Where A is the number of bacterial colonies from the treated specimen after inoculation over 24 hours of the contact period, and B is the number of bacterial colonies from the untreated specimen after inoculation at zero contact time.

IR spectroscopy

IR spectra of unmodified and selectively modified silk samples were obtained following the KBr pellet technique by using a Perkin-Elmer FT-IR spectrometer. The dried fibre samples were crushed to a finer size up to 20 meshes before palletizing with KBr. Four KBr pellets contained about 1% powdered fibres as test specimens were prepared separately for unmodified eri silk and eri silk modified with maleic acid in presence of different catalytic systems as specified (Das et al. 2011).

Scanning Electron Microscopy analysis

Morphological analysis of composite fabric is carried out by Scanning Electron Microscopy (SEM), (JEOL JSM-6510LV) at a magnification of 1000X. Samples were sputter-coated with gold before the measurement.

Results And Discussion

Effect of dual catalyst on the maleic acid cure of eri silk fabric

To study the role of esterification catalyst and free radical polymerization catalyst for the pad-dry-cure technique of silk fabric with maleic acid, the silk fabric was treated with maleic acid in absence of either of the two catalysts with varying concentrations of *Aloe vera* gel @ 5% to 15% (w/v), (see table 2). In each experiment maleic acid dose levels were maintained at 10% (w/w). Treatment of silk fabric in the presence of peroxodisulfate as the free radical polymerization catalyst only resulted in poor weight gain and wrinkle recovery angle with retention of a high order of tensile strength. Such effects appear to be the consequence of only graft copolymerization induced by ammonium peroxodisulfate (as shown in the chemical reaction scheme 2.a. (i) and (ii), 2.b. and 2.c. In Figure 1 in the introduction section) and limited self catalyzed esterification reaction effected only at a high temperature of drying and curing. Silk fabric finished with maleic acid in presence of only esterification catalyst also resulted in poor weight gain with only marginal improvement in wrinkle recovery angle with high retention of tensile strength inconsequent to the establishment of ester linkages under the influence of esterification catalyst (as shown in reaction scheme 1 in Figure 1) with limited thermally induced graft copolymerization of maleic acid in absence of free radical polymerization catalyst. Under the influence of two catalysts taken together (ammonium persulphate and trisodium citrate) for the maleic acid cure of silk, substantial weight gain and wrinkle recovery angle is achieved. Retention of tensile strength, however, suffers for the maleic acid cure of silk under the influence of dual catalyst system was noted in our study. However, to increasing the antimicrobial efficiency, the tear strength and tensile properties were brought down due to a reduction in chain flexibility after graft polymerization under dual catalytic effect at higher temperature curing. Although the crease recovery angle was increased to some extent at an initial concentration of *Aloe vera* gel up to 10% (w/v) and thereon, it started decreasing as the flexibility of chain molecules reduces at a higher concentration of *Aloe vera* gel i.e. 15% (w/v) and so on. Results in Table 2, clearly shows the retention or improvements in weight gain, wrinkle recovery angle and tensile strength are optimal on pad-dry-iron-cure of silk with maleic acid under the influence of a dual catalyst system.

Effect of variation of batching time and pH variation

In each experiment, the maleic acid dose level was maintained at 10% (w/w) for batching at 30^0C room temperature for 60 minutes. In the case of the dual catalyst system and subsequent drying by heating at 95^0C for 5 minutes, followed by curing at 140^0C for 5 minutes, there is a notable weight gain, wrinkle recovery angle, tear strength retention, breaking load retention and elongation at break. However, bending length remained level for the entire batching time. The batching for an extended time distinctly favour higher incorporation of maleic acid moieties on silk by ammonium persulphate induced graft copolymerization. Initial peroxodisulfate induced homopolymerization of maleic acid, to increase extents over increasing batching periods, at ambient temperature 30^0C and further polymerization of free maleic acid and silk bound maleic acid moieties during subsequent drying at 95^0C cause an overall change in environment and proximity of the hydroxyl groups of silk and carboxyl groups of the unbound or silk bound maleic acid or poly (maleic) acid moieties that finally causes an enhanced degree of trisodium citrate catalysed esterification and further chain polymerization leading to substantial cross-linking during curing at 140^0C as revealed by the relevant data for wrinkle recovery in Table 3.

The esterification reaction that assumes more prominence at the high processing temperature (140^0C) in the final stage appears to be somewhat dependent on the initial batching time. An increase in batching time favours improved transformation of the grafted maleic acid /poly (maleic) acid units to ester moieties at the high curing teperature140^0C under the influence of the esterification catalyst in the final stage of processing. Optimum batching time (45-60) minutes also allows improved diffusion of finishing agent maleic acid within the chain molecules of silk.

Relevant data for the change of pH indicate that under neutral condition (pH 7), optimum grafting and esterification leading to much-improved wrinkle angle and substantial weight gain are achieved with no loss of breaking strength and with more than 90% retention of tear initial fabric. In the case of the moderate acidic condition, (pH 5.6), moderate improvement in extensibility with more than 80% retention of the tear strength of the initial fabric was achieved.

Again, moderate alkaline conditions, (pH 8-9) result in poor retention of breaking strength (<70%), and tear strength(<75%), despite substantial weight gain much as a consequence of weakening of the silk fibre in the fabric by alkali attack. Under the slightly acidic condition, (pH 5.6), improvement in wrinkle recovery angle is comparatively poor even though tear strength and breaking strength retention are good, (pH 7), therefore, apparently provides the most optimum condition of the finishing process.

The antibacterial activity was quantitatively assessed against gram-negative bacteria viz. E. coli: Strain No. ATCC 9637 and gram-positive bacteria viz. S. aureus: Strain No. ATCC 6538, according to the AATCC 100-2004 test method. The bacterial reduction percentage (%) of the treated eri silk fabric against gram-negative E. coli and gram-positive S. aureus on treated fabric with 10% (w/v) *Aloe vera* gel is observed to be 97 and 91, respectively. The results of IR analysis suggests that esterification of maleic acid with the hydroxyl group of silk effectively accomplished in presence of trisodium citrate and free radical polymerization with simultaneous grafting of poly (maleic acid) on silk effective accomplished in presence of ammonium persulphate on pad-dry-cure of maleic acid-treated silk fabric. In the presence of two catalysts during maleic acid treatment both the reaction became prominent resulting in cross-linking of protein molecules promoting wrinkle recovery of silk.

It is also noteworthy that since more cross-linking takes place when the reaction between the fibres and maleic acid is more active with a higher power or longer time, the treated fibres become hardened and straightened, resulting in a greater loss of tensile strength of fabrics. Furthermore, long time enhances the hydrolysis of fibres in acid catalysts thereby reducing the tensile strength of the finished eri silk fabric.

This work is aimed at establishing optimum condition for the application of maleic acid evaluating attainable changes or improvements in the fabric nature and properties including crease-resistance, stiffness, strength, and moisture regain anti-microbial, properties. Results of such studies are reported in the present article.

Effect of Aloe vera gel concentration

Figure 2 shows the effect of *Aloe vera* gel concentration from 5-15% (w/v) on the performance properties of eri silk, viz., wrinkle recovery angle and tear and tensile strength of the treated fabric. The finishing baths were prepared to contain Ammonium persulphate 1% and trisodium Citrate: 6%, the fabrics treated thus with 100% pick up were dried and then exposed to curing at 140^0C for 5 minutes. It is clear (Figure 2) that the wrinkle recovery angle of the treated fabrics which were cured was pronounced as *Aloe vera* gel concentration increased up to 10% (w/v) and then decreased sharply whereas, there was a notable increase in weight gain with the increase of dose level of *Aloe vera* gel concentration.

The enhancement in wrinkle recovery angle of the finished fabrics by increasing *Aloe vera* gel concentration suggests that *Aloe vera* gel performed two functions: (1) it reacts with maleic acid in the fibre molecules; (2) *Aloe vera* gel undergoes cross-linking with the fabric to form a network matrix. The water-soluble *Aloe vera* gel with its low molecular weight penetrates the fibre more easily promoting anti creasing in the treated eri silk fabrics. Water-soluble *Aloe vera* gel generates an ether reaction with the hydroxyl groups in the fibres, forming a two-dimensional structure that improved the crease resistance of the fabrics. Decrement in wrinkle recovery angle by increasing the *Aloe vera* gel concentration above 10% (w/v) could be associated with increased basicity of the finishing environment at higher *Aloe vera* gel concentrations. Logically, basicity would stand as an inverse function to the acidity of the catalytic system of the cross-linking peptide molecule with maleic acid under the dual catalytic influence. Lower catalysis would certainly lead to decreased wrinkle recovery angle. With respect to tensile strength, on the other hand, penetration or encapsulation of *Aloe vera* gel molecules would improve the strength properties of the treated fabrics. As shown in Figure 2, the tensile strength and elongation at break increased by increasing *Aloe vera* gel concentration up to 10% (w/v) which tends to decrease thereafter. Rigidity conferred on the structure of silk by the inclusion of *Aloe vera* gel through various interactions with silk and maleic acid may account for the decrease in tensile strength at higher *Aloe vera* gel concentrations and also, tear strength retention shows a monotonic fall with increases of *Aloe vera* gel dose level. It is also probable that higher concentrations of *Aloe vera* gel n create more fibres bridging and are more likely to cause stress accumulation thereby decreasing the tensile strength. Breaking load increased by increasing *Aloe vera* gel concentration up to 10 g/1 which tends to decrease thereafter. Rigidity conferred on the structure of silk by the inclusion of *Aloe vera* gel through various interactions with silk and maleic acid may account for the decrease in tensile strength at higher *Aloe vera* gel concentrations and also, tear strength retention shows a monotonic fall with increases of *Aloe vera* gel dose level. It is also probable that higher concentrations of *Aloe vera* gel create more fibres bridging and are more likely to cause stress accumulation thereby decreasing the tensile strength.

Pore size analyser of treated and untreated sample

Pore Size Analyser Report like smallest pore diameter (micron), largest pore diameter (micron), mean flow pore diameter (micron), as well as first bubble point diameter (micron), is given below in Table 4.

The distilled water of surface tension 72 mN/m was used for wetting the samples and test pressure was kept at 0.5 bar. The smallest and largest flow pore size of the untreated sample was measured as 7.89 and 336.21 micrometres, respectively. The smallest and largest flow pore size of the treated sample were found as 7.68 and 332.22 micrometres, respectively when the sample is treated with 5% *Aloe vera* gel. The mean pore diameter was found 232.52 micrometres for the same sample. The smallest and largest pore size of the treated sample with 10% *Aloe vera* gel was found to be 7.55 and 321.28, respectively and the mean pore diameter was observed as 219.03 micrometres. It is observed that there is a slight decrease in the mean pore diameter after-treatment of the 5% *Aloe vera* gel and the decrement is more significant after the treatment of the 5% *Aloe vera* gel. This may be attributed due to the add-on of mass on the fibre surface blocking the pores. The presence of the *Aloe vera* coating on the fibre surface can be evidenced by SEM images.

Evaluation of antibacterial property of textile fabric:

The antibacterial activity was quantitatively assessed against gram-negative bacteria E. coli: Strain No-ATCC 9637 and gram-positive bacteria S. aureus: Strain No-ATCC 6538), according to the AATCC 100-2004 standard test method. The test microorganism is grown in liquid culture. The concentration of the test microorganism is standardized. The microbial culture is diluted in a sterile nutritive solution. Untreated and treated fabric swatches are inoculated with microorganisms. The inoculation is performed such that the microbial suspension touches only the fabric. Bacteria levels on both untreated and treated fabrics are determined at 'time zero' by elution in a large volume of neutralizing broth, followed by dilution and plating. A control is run to verify that the neutralization/elution method effectively neutralizes the antimicrobial agent in the fabric. Additional inoculated control and test fabrics are allowed to incubate, undisturbed in sealed jars, for 24 hours. After incubation, microbial concentrations are determined. Reduction of microorganisms relative to initial concentrations and the control fabric is calculated. Per cent reduction of bacteria by the specimen treatments was calculated using the following formula: $R= 100 (B – A)/B$ where R is % reduction A is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over desired contact period. B is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation (at '0' contact time).

The inoculation is performed such that the microbial suspension touches only the fabric. The photographs of bacterial growth on untreated and maleic acid-treated samples in presence of *Aloe vera* gel with varied concentration i.e. 5% (w/v) and 10% (w/v) under dual catalytic effect are also given in Figure 3.

Maleic acid treatment when suitably done with *Aloe vera* gel caused a substantial reduction in the growth of microorganism in treated samples assessed in terms of colonies recovered. The finished is normally tested for antibacterial properties and finish stability is tested even after 10 washing cycle after washing the fabric with non-ionic detergent at mild Alkaline PH. From the result, it can be inferred that the eri silk fabric finished with *Aloe vera* showed more than 90% antimicrobial property against both the bacteria. Even after 10 wash, it shows more than 80% antimicrobial efficiency. This may be due to significant loss of active ingredient of *Aloe vera* after 10 machine washes. In other words, cross-linking are deteriorated paving the way for the active ingredients to leach out from the fabric during washing.

FTIR analysis

The FTIR spectra of untreated silk fabric and eri silk treated with maleic acid and *Aloe vera* gel under conventional curing are shown in Figure 4. A broad absorption band over 3200 cm^{-1} characteristic of hydrogen-bonded (N-H) stretching vibration and an absorption band in the range of 1621 cm^{-1} to 1637 cm^{-1} characteristic of amide stretching are common to all spectra (Das *et al.,* 2014). Two notable absorption bands at 1316.14 cm^{1} and 1426.65 cm^{-1} appearing in different intensities in the spectrum of unmodified silk [spectrum 1 of Figure 4] are characteristic of carboxylate anion stretching and phenolic (-OH) bending, respectively. Carboxylate anion stretching accounts for the presence of a free carboxylic acid group at the end of polypeptide chains and phenolic (-OH) bending accounts for the presence of residues of tyrosine fractions of amino acids in the unmodified silk. The strong absorption band at 1202.68 cm^{-l} and 1156.89 cm^{-l} also appears in the spectrum of unmodified silk and is attributed to (C-N stretching) vibration of amine groups present at the end of polypeptide chains of silk. In the spectrum of unmodified silk, the absorption band at 1621.16 cm^{1} (ester stretching) and 962.44 cm^{-1} (vinyl un-saturation) are practically not existent.

The maleic acid finish on eri silk in presence of esterification catalyst i.e. trisodium citrate only however result in intensification of the absorption band at 1510.19 cm^{-1} characteristics of vinyl ester stretching (spectrum 4 in Figure 4), substantial weakening of absorption band at 1510.19 cm^{-1} characteristic of unsaturation present in the vinyl group as expected (spectrum 5 in Figure 4). However, maleic acid finish on eri silk under the influence of dual catalyst system (spectrum 4 of Figure 4) results in weakening of the band at 1023.74 cm^{-1} due to significant disappearance of the vinyl group unsaturation during final stage polymerization induced by heat and catalyst action along with sharp intensification of the band at 1621.14 cm^{-1} due to stretching with retention of the band corresponding to 1426.65 cm^{-1} for carboxylate (anion) stretching. Silk treated with maleic acid and *Aloe vera* gel (spectrum 5) exhibited a decrease in absorbance intensity at 1636.69 cm^{-1} and 1426.65 cm^{-1} after the curing method as compared with untreated silk sample. A decrease in intensity at 1636.69 cm^{-1} and 1426.65 cm^{-1} could be attributed to a decrease in the total number of hydroxyl groups through crosslink formation between silk and maleic acid. Substantial weakening/disappearance of band 1426.65 cm^{-1} corresponded to phenolic (-OH) bending due to significant disappearance of phenolic (-OH) groups. Silk Proteins are known to attach to *Aloe vera* gel through carboxylate ions which show antimicrobial potential. The results of the IR analysis are in tune with the mechanism proposed.

FTIR spectra of treated fabric showed that the intensity of this band is a measure of the total quantity of ester group created in the finished eri silk fabrics. The FTIR spectrum (spectrum 4 and 5 of Figure 4) of *Aloe vera* treated fabric showed a little shift of ester peak from 1623.50 (spectrum 4 of Figure 4) cm-1 to 1621.16 cm-1 (spectrum 5 of Figure 4) and also the intensity of this peak is lowered as compared to that of only maleic acid-treated fabric (spectrum 4 of Figure 4). This indicates a decrease in the average number of ester groups formed in presence of *Aloe vera*. The lower intensity peak of *Aloe vera* with cross-linking agent treated eri silk is due to the interaction of *Aloe vera* active compounds with some of the amine (-NH) groups of the eri silk and also interaction with the free –COOH groups of carboxylic acid molecules which are supposed to form ester linkage with eri silk in absence of *Aloe vera* compounds. Hence, the extent of degree of direct chemical cross-linking between eri silk and maleic acid via ester linkage is effectively less in *Aloe vera* treated samples as some of the –NH groups of eri silk are actively occupied by some of the – OH groups of *Aloe vera* ingredients. Thus active ingredients of *Aloe vera* containing –

OH groups in their chemical structure can easily form H-bonding with the either –NH groups of eri silk structure or chemically react with the maleic acid during curing of *Aloe vera* and silk molecules.

SEM Image Analysis

Surface deposition of finishing chemicals is depicted below in Figure 5 using the following SEM image.

Figure 5 shows SEM images (a) untreated degummed silk (b) degummed silk treated with 5% *Aloe vera* gel (c) degummed silk treated with 10% *Aloe vera* Gel. In the SEM image of untreated degummed silks, the smooth well-separated filament of degummed silk appears with no surface deposition of any chemical agent. However, fibrillation of silk fibroin affected due to the degumming treatment can be traced in some portion of the silk fibre in the SEM of the degummed silk. Treatment of silk with 5% *Aloe vera* gel resulted in the deposition of *Aloe vera* gel on the surface of the silk fibre as seen in the micrograph b. Such deposition of *Aloe vera* gel as appears in micrograph b, however, is less frequent, few and incapable of giving uniform distribution of such *Aloe vera* gel on the surface of the silk. Silk when treated with 10% *Aloe vera* gel shows a much more uniform and frequent distribution and presence of *Aloe vera* gel that covers almost all the surface area of the silk fibres which however retained by the silk fibre even when the silk was post washed following a method described in the experimental section. *Aloe vera* gel retained by the silk fibres appears to be capable of conferring antimicrobial properties to the silk fibres. And the extent of such functional properties offered by the silk fibres in our experiment reported in this study appears to be in line with the deposition of *Aloe vera* gel in consequence of the different treatment of *Aloe vera* gels described in the present study.

Conclusions

Aloe vera has been used for medicinal and cosmetic purposes because of its natural antibacterial properties. *Aloe vera* as a finish applied on eri silk fabrics to impart antibacterial properties has been reviewed. Out of all the methods of application of *Aloe vera* antibacterial finish to eri silk, the pad-dry-cure method is the most widely used. It is the most viable method to give antibacterial finishes to textile materials in an eco-friendly manner. Fabric treated with 100% concentration of *Aloe vera* extract at 10% (w/v) concentration, processed for 10–15 minutes at 90^{0}C showed optimum antibacterial properties as compared to other concentrations. The washing durability was found to be good by this method. To increase the stability of antibacterial finish chitosan were used as a binding agent in finishing. Although the availability of *Aloe vera* is in bulk quantities, their extraction, isolation and purification to get standardized products are some of the challenges in their application. Also, shelf life and antimicrobial efficacy are other issues that need to be considered. However, because of their eco-friendly nature and non-toxic properties, they are still promising candidates for niche applications in textile. It was observed that with the increase in the per cent of *Aloe vera* gel concentration the bacterial reduction increases. The treated fabric retains antibacterial activity for many washes.

The appropriate maleic acid finish on silk in presence of *Aloe vera* gel with varied concentrations under neutral condition establishes a formaldehyde-free route for achieving simultaneous core and surface modification of silk with high scope for incorporation of much improved physical and mechanical properties for the fabric.

The major properly advantages that can be derived from the maleic acid finish by following the maleic acid pad-dry-cure technique under the dual catalytic influence of trisodium citrate and ammonium persulphate are substantial improvements in (i) wrinkle recovery, (ii) extensibility and (iii) moisture regain, (iv) anti-microbial properties with associated retention of a high order of tensile and tear strength.

Declarations

Competing interests: The authors declare no competing interests.

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Tables

Table 1.: The composition of different type of silk

	Mulberry silk	Tasar silk	Muga silk	Eri silk
Fibroin (%)	70-80	80-90	80-90	80-90
Sericin (%)	20-30	8-10	8-10	4-5
Other (%)	2-3	3-5	3-5	3-5

Table 2. Effect of dual catalyst system for the maleic acid cure of silk.

Ammonium persulphate	Trisodium citrate	*Aloe vera*	Application of PH	Weight gain%	Wrinkle Recovery Angle	Tearing strength retention (%)	Breaking Load (N cm^{-1})	Elongation at Break (%)	Bending Length (cm)
0%	10%	5%	7	6.61	215	75	31	14	1.60
1%	0%	5%	7	8.55	204	78	39	19	1.65
1%	10%	5%	7	9.64	254	86	42	13	1.70
0%	10%	10%	7	6.62	217	77	30	13	1.70
1%	0%	10%	7	7.57	205	81	37	18	1.70
1%	10%	10%	7	8.15	257	90	42	15	1.80
1%	10%	15%	7	9.24	249	81	39	13	1.80
Silk untreated		–	–	175	100	43	17	1.60	

Table 3. The effect of variation of Batching Time and pH on different physical and mechanical properties of degummed silk.

Ammonium persulphate	Sodium tricitrate	Application of pH	Weight gain%	Wrinkle Recovery Angle $(w+f)^0$		Tearing strength retention (%)	Breaking load (N cm^{-1})	Elongation at break (%)	Bending length (cm)
				Dry	Wet				
(A) Effect of variation of pH									
+	+	5	3.16	218	248	80%	43	17	1.70
+	+	6	3.84	228	257	83%	43	18	1.70
+	+	7	8.15	252	262	90%	44	15	1.80
+	+	8	8.36	254	269	72%	32	14	1.80
+	+	9	8.55	240	266	69%	30	13	1.80
+	–	7	4.67	222	229	76%	32	19	1.70
(B) Effect of variation of batching time									
++	0	7	4.39	193	210	85%	40	17	1.60
++	30	7	5.29	228	263	86%	42	18	1.65
++	45	7	6.78	251	274	90%	43	19	1.70
++	60	7	8.05	258	281	91%	45	20	1.80
(C) Degummed silk	–	–	–	175	186	100%	43	17	1.60

Maleic acid: 10%; Ammonium per sulphate: 1%, Trisodium citrate: 6%, Aloe vera gel 10% (w/v), Drying at 95^{0}C, Curing at 140^{0}C for 5 minutes; w+ f □ warp and fill.

Table 4. Pore Size Analyser Report

Flow Pore Diameter (Micron)	Untreated Sample	Treated sample with 5% *Aloe vera* gel	Treated sample with 10% *Aloe vera* gel
Smallest Flow Pore Diameter (Micron)	7.89	7.68	7.55
Largest Flow Pore Diameter (Micron)	336.21	332.22	321.28
Mean Flow Pore Diameter (Micron)	234.71	232.52	219.03
First Bubble Point Diameter (Micron)	691.15	620.30	618.30

Figures

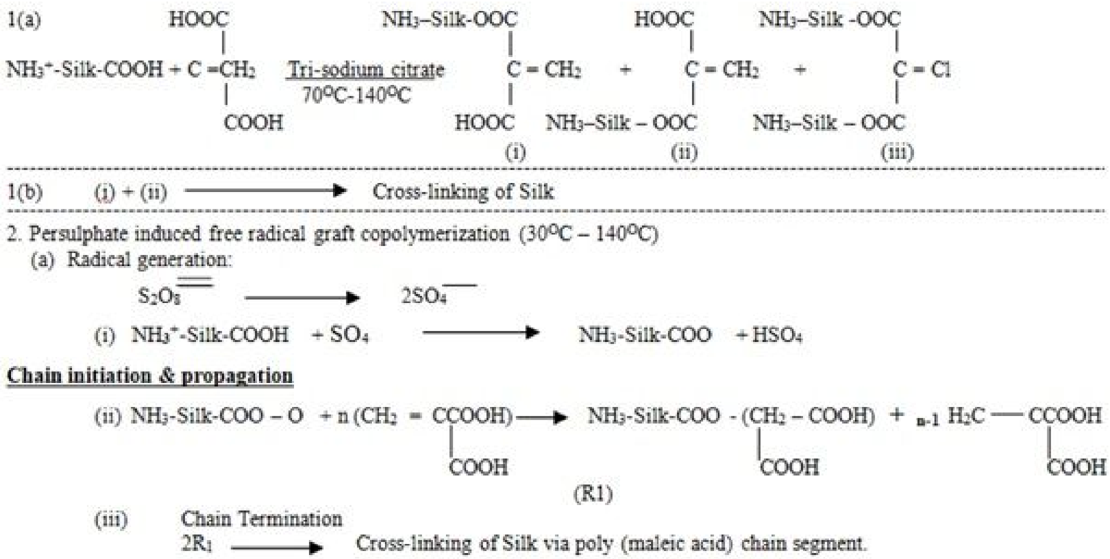


Figure 1

The chemical reaction for modification of silk fibre

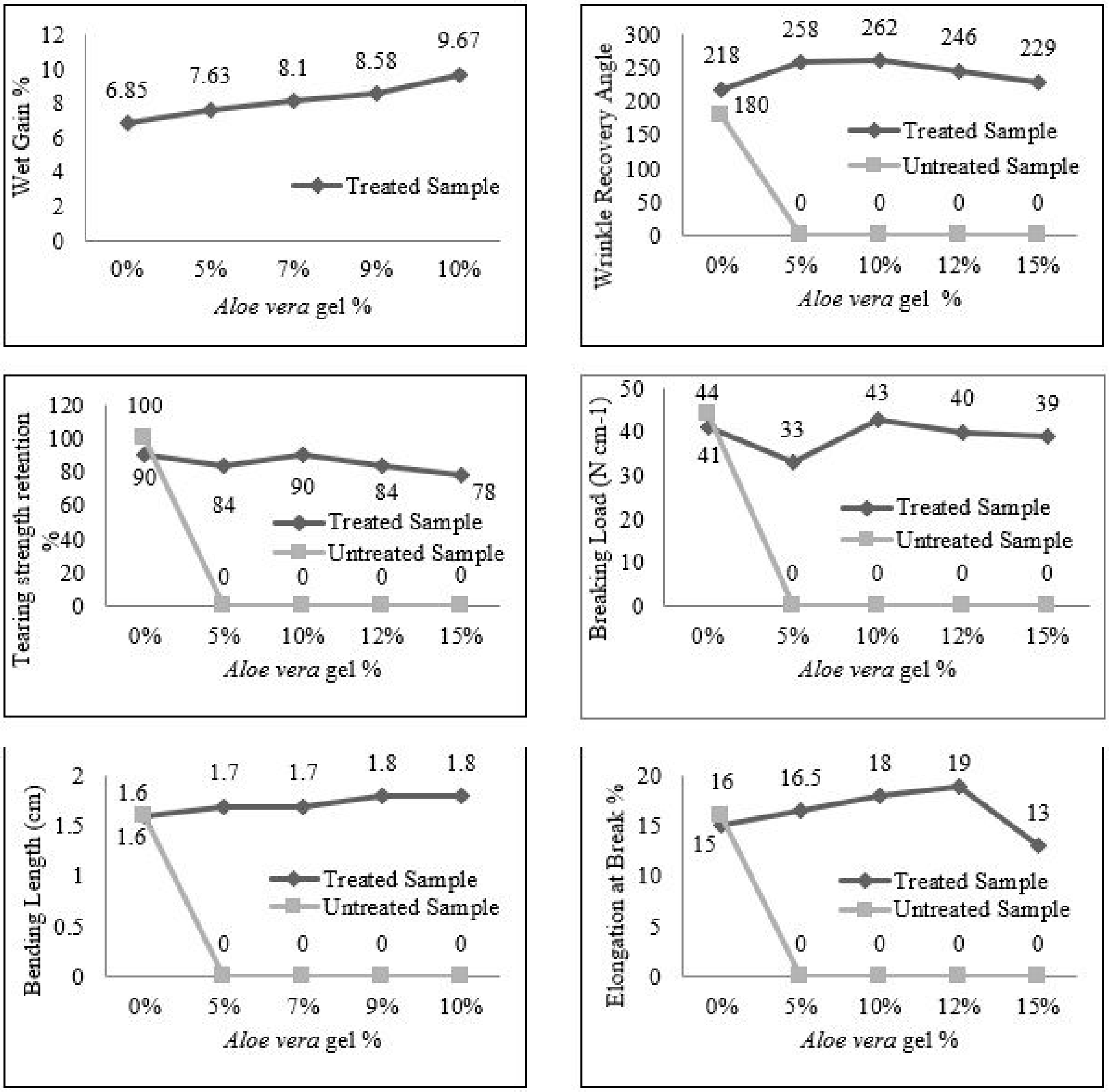


Figure 2

Effect of Aloe vera gel concentration on maleic acid finished eri silk

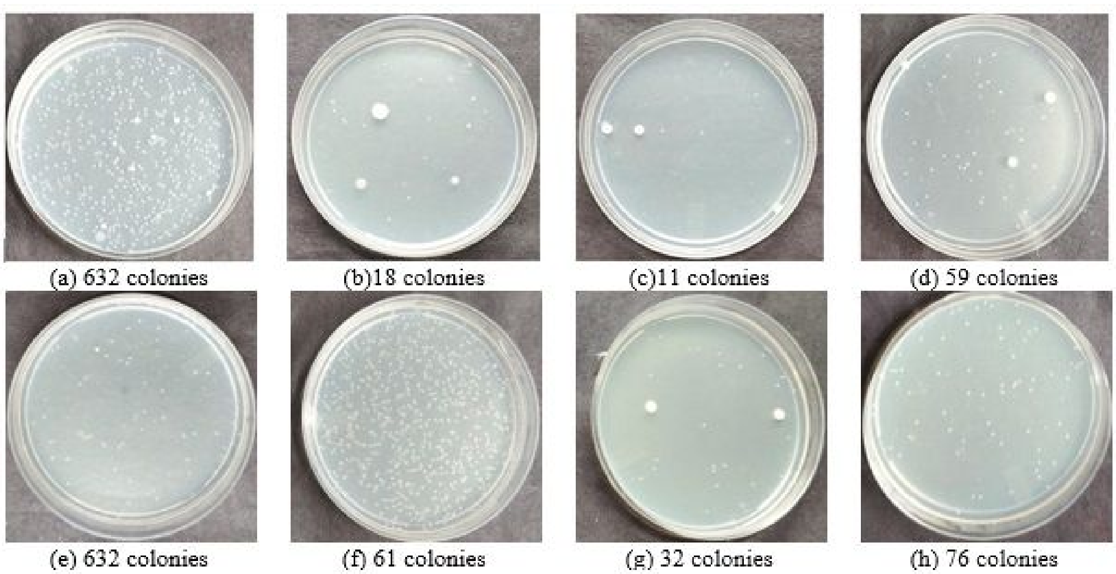


Figure 3

Photographs of development of different bacterial growth (a) E. coli on untreated eri silk (b) E. coli on treated eri silk with 5% (w/v) Aloe vera gel concentration (c) E. coli on treated eri silk with 10% (w/v) Aloe vera gel concentration (d) E. coli on treated eri silk with 10% (w/v) Aloe vera gel concentration after 10 wash cycle; (e) S. aureus on untreated eri silk (f) S. aureus on treated eri silk with 5% (w/v) Aloe vera gel concentration (g) S. aureus on treated eri silk with 10% (w/v) Aloe vera gel concentration (h) S. aureus on treated eri silk with 10% (w/v) Aloe vera gel concentration after 10 wash cycle.

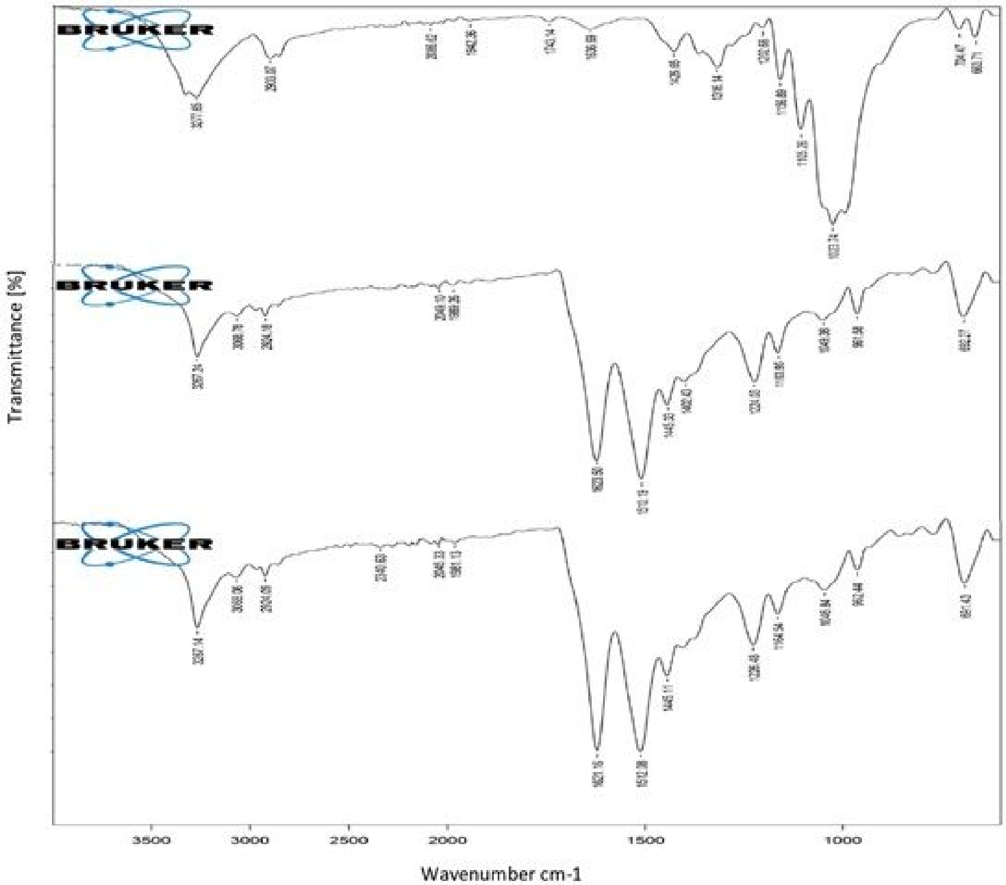
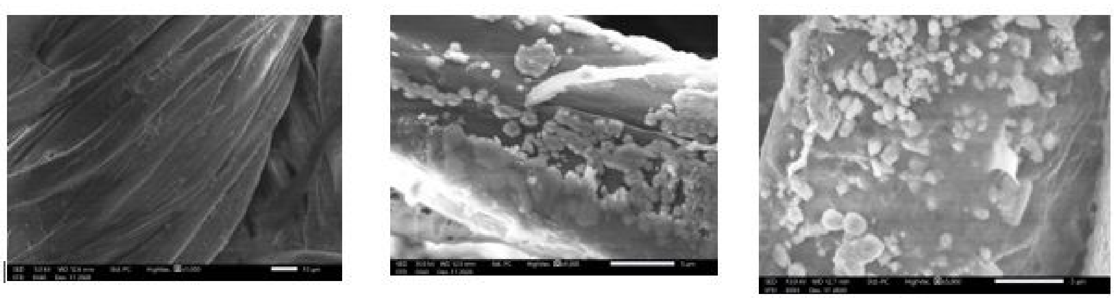


Figure 4

IR spectra of 1) unmodified eri silk, 2) modified eri silk with maleic acid in the presence of trisodium citrate and ammonium persulphate (3) modified eri silk with maleic acid in the presence of trisodium citrate and ammonium persulphate and Aloe vera gel.



(a).Untreated eri silk fabric. (b). Eri silk fabric treated with 5% *Aloe vera* gel. (c). Eri silk fabric treated with 10% *Aloe vera* gel.

Figure 5

SEM image of untreated and treated eri silk fabric